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CHEMICAL REACTION AT HIGH TEMPERATURE AND HIGH PRESSURE VI

Polymorphic Transition in ZnP_2 at High Temperature and High Pressure

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A new pressure-induced modification of zinc-diphosphide, ZnP_2, has been prepared by the direct union of zinc with phosphorus and also through the polymorphic transitions of both monoclinic and tetragonal ZnP_2. The application of pressures above 20 kb combined with temperatures above 150°C is required for the synthesis. The new modification of ZnP_2 has a pseudo-cubic crystal symmetry with a lattice constant $a=5.322$Å and has a measured density 3.55 g/cm³. It is found to be a semiconducting phase with an energy gap $E_g=0.44$ eV at 15 kb in the temperature range from 20° to 150°C. The effects of temperature and pressure on the polymorphic transition of monoclinic and tetragonal ZnP_2 have been investigated and the stability region for the high pressure modification determined by quenching method. The synthesis of a diamond-like form of ZnP_2, which is one of II–V_2 type compounds, suggests the possibility of synthesizing other unsymmetrical group IV analogs which was predicted by Hall and Compton earlier.

Introduction

As for the binary systems of group II and V elements, several compounds with the formulas A_3B_2 and AB_2[1] have been known. The existence of AB_4 type compounds was also confirmed both in the Cd-P[2] and the Mg-As[3] systems.

In the Zn-P system there exist three semiconducting compounds: tetragonal Zn_3P_2[1], tetragonal ZnP_2[1] and monoclinic ZnP_2[4]. Renault[5], however, reported in 1866 that yellow amorphous ZnP_4 was obtained by treating a large amount of Zn_3P_2 with aqueous HCl, H_2SO_4 or HNO_3. Tetragonal Zn_3P_2 has a composition expected from the normal valence rule. The kinetics of solid state reaction of zinc with phosphorus to form Zn_3P_2 under high pressure was described in the preceding paper.

The tetragonal and the monoclinic ZnP_2 have an anomalous composition which differs from that expected from the normal valence rule. In ZnP_2, each atom has tetrahedrally coordinated sp^3 bondings since the average number of valence electron per atom is 4. In order to saturate the valences the anoma-

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1) M. V. Stackelberg and R. Paulus, *Z. physik. Chem.*, **B28**, 427 (1935)
2) H. Krebs, K. H. Müller and G. Zürn, *Z. anorg. allg. Chem.*, **285**, 15 (1956)
3) K. Pigon, *Helv. Chim. Acta*, **44**, 30 (1961)
4) I. J. Hegyi, E. E. Loebner, E. W. Poor, Jr. and J. G. White, *J. Phys. Chem. Solids*, **24**, 333 (1963)
5) Renault, *Ann. Chim. Phys.*, **9**, 168 (1866)

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lously composed semiconductors[6][7] have the cation-cation or the anion-anion bonds besides the cation-anion bonds. Although the crystal structures of binary intermetallic compounds which have tetrahedrally coordinated sp^3 bondings are generally assigned to the sphalerite or the wurtzite structure, two modifications of ZnP_2 belong to neither of them.

In recent papers we reported the occurrence of new pressure-induced modifications in the Si-P[8], the Ge-P[9] and the Sn-P[9] systems and it was predicted that some anomalously composed semiconductors, in which a sort of atom has more than two independent crystallographic sites, will produce new high pressure modifications when the reactions are undertaken at high temperature under very high pressure since high pressure makes higher the coordination number and the crystal symmetry.

From the wide interest in anomalously composed ZnP_2, the effects of pressure on the crystal structures of two modifications of ZnP_2 have been investigated at 50~800°C under 5~50 kb. It is also the purpose of this work to attempt the synthesis of new crystalline modifications of ZnP_4 at high temperature and high pressure.

Experimentals

Materials

Extra pure zinc and red phosphorus were obtained commercially. The monoclinic and the tetragonal ZnP_2 were synthesized from zinc and red phosphorus directly in the following way. Using the Zn : P=1 : 2 starting mixture the monoclinic ZnP_2 and a small amount of Zn_3P_2 were prepared at about 450°C and pressures of 10~12 kb. The monoclinic ZnP_2 and unreacting phosphorus were isolated from Zn_3P_2 and unreacting zinc by treating with aqueous HCl since monoclinic ZnP_2 and phosphorus are resistant to HCl while Zn_3P_2 and zinc are attacked easily. Unreacting phosphorus intermixed in the monoclinic ZnP_2 was converted into Zn_3P_2 by repeating the reaction and removed in the similar way. Thus pure monoclinic ZnP_2 was obtained. The tetragonal ZnP_2, which is not attacked by HCl either, was prepared by the similar reaction at about 1,000°C under 13 kb and the same procedures. The homogeneity of the monoclinic and the tetragonal ZnP_2 was confirmed by means of X-ray diffraction. It was also confirmed that the specimens were oxidized completely with aqueous HNO_3. If there exists phosphorus in the specimen it remains unreacted with aqueous HNO_3.

High pressure technique and procedures

A Bridgman type piston-cylinder apparatus[10] was used to prepare the samples of the monoclinic and the tetragonal ZnP_2. A compact cubic anvil apparatus[11][12] was also used to investigate the phase transition of ZnP_2 at high temperature and high pressure. The specimen was placed inside the glassy

6) F. Hulliger and E. Mooser, *J. Phys. Chem. Solids*, **24**, 283 (1963)
7) W. B. Pearson, *Acta Cryst.*, **17**, 1 (1964)
8) J. Osugi, R. Namikawa and Y. Tanaka, *This Journal*, **36**, 35 (1966)
9) J. Osugi, R. Namikawa and Y. Tanaka, *ibid.*, **37**, 81 (1967)
10) J. Osugi, K. Shimizu and Y. Tanaka, *Proc. Japan Acad.*, **40**, 105 (1964)
11) J. Osugi, K. Shimizu, K. Inoue and K. Yasunami, *This Journal*, **34**, 1 (1964)
12) J. Osugi, K. Shimizu and Y. Tanaka, *Proc. Japan Acad.*, **42**, 48 (1966)

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carbon tube directly without a pyrophyllite sheath. A chromel-alumel thermocouple was used for temperature measurement. The phase transition was detected by recovering the specimen to the normal condition and by analysing it by X-ray diffraction. Ni-filtered Cu-kα radiation was used. The (111) peak of the pseudo-cubic pressure-induced modification of ZnP_2 was utilized for detecting the phase transition.

Electrical resistance measurements

The measurements of electrical resistance at high temperature and high pressure were made on the powdered samples in the cell devised by Onodera *et al.*[13] The pyrophyllite cube contained a 6mm diam. glassy carbon heater, in which a 4mm cylinder of pyrophyllite was placed. The specimens were placed at the center of the pyrophyllite cylinder. Two anvils afforded electric contact to the sample through platinum foils. Another two anvils afforded electric contact to the glassy carbon heater through copper wires. The temperature was monitored by means of chromel-alumel thermocouples. The resistance measurements were made by using a TOA PM-8 type vacuum tube voltmeter.

Table 1 Data of X-ray diffraction diagrams for tetragonal ZnP_2

d (Å)	I/I_0		hkl
	orange	red	
4.647	40	18	004
3.929	3	3	103
3.527	13	15	111
3.429	75	100	104
3.351	75	100	112
3.108	5	10	113
3.000	7	13	105
2.842	25	44	114
2.517	9	8	201
2.350	20	31	203
2.324	100	50	008
2.255	3	5	211
2.229	10	18	204
2.207	20	40	212
2.133	5	7	213
2.094	10	11	205
2.041	5	6	214
1.9386	20	33	215
1.8321	30	50	216
1.7877	7	7	221
1.7635	6	25	222
1.7222	4	4	223
1.6753	11	20	224
1.6659	6	3	302

13) J. Osugi, K. Shimizu, T. Nakamura and A. Onodera, *This Journal*, 36, 59 (1966)

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Experimental results

Crystal structures and characteristics of two modifications of ZnP_2

The data of X-ray diffraction diagrams for the monoclinic and the tetragonal ZnP_2 obtained in the present work are given in Tables 1 and 2. The unit cell dimensions are as follows.

tetragonal ZnP_2 $a=5.08$Å, $c=18.59$Å

monoclinic ZnP_2 $a=8.85$Å, $b=7.29$Å, $c=7.56$Å, $\beta=102°$.

These data are in good agreement with those reported by White *et al.*[4)14)].

The tetragonal ZnP_2 is a red~orange colored semiconductor with resistivity of $10^8\,\Omega$-cm and optical energy gap of 2.05 eV, which were measured by White *et al.*[4)] on the single crystal at atmospheric pressure. All the atoms are tetrahedrally coordinated. It is a characteristics of the tetragonal modification that it has the anion-anion (P-P) bonds besides the cation-anion (Zn-P) bonds.

The monoclinic ZnP_2 is a black-greenish semiconductor with resistivity of $10\,\Omega$-cm and optical energy gap of 1.33~1.37 eV. The unit cell contains eight formula units. Although all the atoms are tetrahedrally coordinated like as in the tetragonal ZnP_2, the crystal structure is much complicated and has a lower symmetry since both the anion-anion (P-P) and the cation-cation (Zn-Zn) bonds occur besides the cation-anion bonds in this modification.

Under atmospheric pressure, the synthesis of ZnP_2 was carried out in a sealed quartz system containing zinc and excess phosphorus as reported by White *et al.*[4)] At one extreme of the tube a temperature about 1,000°C was maintained on the zinc, and at the other extreme phosphorus was heated in the region of 450~500°C so that controlled pressures in the range of 3~10 atm could be maintained throughout the system. For phosphorus pressures of about 3 atm, 50 per cent of the crystal mass was the tetragonal modification, while the remainder was the monoclinic ZnP_2. Phosphorus pressures of about 10 atm gave practically 100 per cent yield of the monoclinic form. However, it was reported that 100 per cent yield of red tetragonal ZnP_2 could not be obtained in any experimental conditions.

Table 2 Data of X-ray diffraction diagrams for monoclinic ZnP_2

d (Å)	I/I_0	hkl	d (Å)	I/I_0	hkl
8.648	4	100	2.681	1	310
5.574	10	110	2.551	17	202, $30\bar{2}$
3.719	45	210	2.409	20	$21\bar{2}$
3.645	4	020	2.339	17	130
3.359	65	120	2.162	4	400
3.294	25	112	2.118	5	230
3.161	100	202	2.095	36	231, $22\bar{2}$
2.900	5	212	2.030	2	$13\bar{2}$
2.883	5	300	1.9902	6	312
2.787	40	220	1.9260	20	232

14) J. G. White, *Acta Cryst.*, **18**, 217 (1965)

On the other hand, it has been confirmed in the present work that only monoclinic ZnP_2 is formed at 500°C under 13kb but it transforms completely into the tetragonal modification at 1,000°C. Therefore, it is possible to obtain 100 per cent yield of tetragonal ZnP_2 at high pressure. The difference between the results obtained at atmospheric pressure and under high pressure may be attributed to the following facts:

1) The measured density of the tetragonal ZnP_2, 3.536 g/cm³ (the calculated density is 3.52 g/cm³) is higher than that of the monoclinic ZnP_2, 3.47 g/cm³ (the calculated density is 3.55 g/cm³).
2) The crystal structure of the tetragonal modification has a much higher crystal symmetry than that of the monoclinic ZnP_2 so that it is more stable under pressures.

The crystal structure of high pressure modification of ZnP_2

As mentioned in the preceding paper[15], Zn_3P_2 once formed at 300°C reacts further with phosphorus to form the monoclinic ZnP_2 in the lower pressure range below 15kb. Above 15~20kb, however, the reaction produces a new high pressure modification. This high pressure modification was also obtained by the direct union of 1Zn and 2P or through the phase transitions of both monoclinic and tetragonal ZnP_2 at high temperature under high pressure. These experiments prove that the new substance has the composition ZnP_2 and is a new crystalline form of ZnP_2.

The X-ray diffraction patterns for the monoclinic and the high pressure forms of ZnP_2 are shown in Fig. 1. This high pressure modification was prepared from stoichiometric quantities of the elements at about 1,000°C under 40kb. The main reflections can be indexed on the basis of a cubic crystal with a lattice constant of $a=5.322$Å. Although other reflections can not be indexed on the same cubic basis.

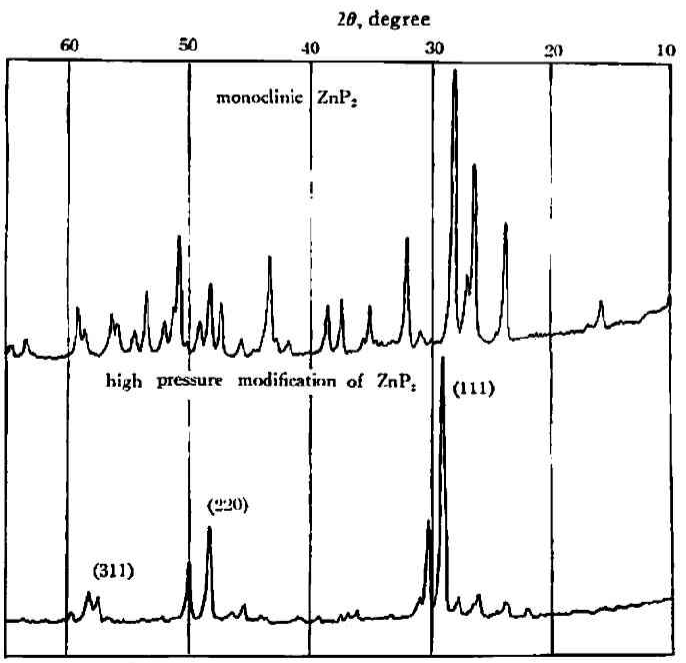

Fig. 1 X-ray diffraction patterns for the monoclinic and the high pressure modification of ZnP_2

15) Y. Tanaka, *This Journal*, 38, 137 (1968)

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they always coexist with the main reflections and their intensities change always with those of the main reflections in similar manner. Therefore they may be assigned to the same phase. The X-ray diffraction data for the high pressure modification are given in Table 3.

The table shows that among the indexed reflections all reflections corresponding to the indices $h+k+l=4n+2$ besides those to the indices with mixed integers disappear. This is an extinction rule characteristic to the diamond structure. However, there exist no high pressure modifications of zinc and phosphorus with this structure having a given lattice constant. Therefore, it is presumed that the high pressure modification of ZnP_2 has a disordered sphalerite like structure, which has a little lower crystal symmetry than the disordered sphalerite structure.

I-VII, II-VI and III-V binary semiconductors are composed of the elements symmetrically arranged on each side of the group IV elements in the periodic table and have a sphalerite or wurtzite structure. Recently Hall and Compton,[16] however, have succeeded in preparing the unsymmetrical compound, hexagonal B_2O, as a graphite analog under 50~70 kb at 1,200~1,800°C by reducing B_2O_3 with B or Li and also by oxidizing B with $KClO_3$. They suggested also the possibility of synthesizing other unsymmetrical group IV analogs having the unit formulas such as I-V_3, I_2-VI_3, II-V_2, II_3-VII_2, III_2-VI and III_3-VII.[10)17] The B_2O obtained at high temperature and high pressure is one of the III_2-VI unsymmetrical compounds. It has a hexagonal layer-lattice structure related to graphite with unit cell dimension $a=7.98$ and $c=9.09$Å. The hexagonal B_2O transforms into a diamond-like form under about 120 kb.

Now, ZnP_2 is one of the II-V_2 compounds and so it is easily predicted that it may transform into a diamond-like structure by very high pressure. It is quite interesting that the polymorphic transition

Table 3 Data of X-ray diffraction diagrams for high pressure phase of ZnP_2

d (Å)	I/I_0	hkl	d (Å)	I/I_0	hkl
4.210	3		1.8241	21	
3.723	6		1.6047	8	311
3.414	9		1.5876	10	
3.209	8		1.5488	3	
3.069	100	111	1.3305	2	400
2.950	35		1.3115	2	
2.488	4		1.2210	5	331
2.436	3		1.1750	2	
2.398	3		1.0864	3	422
2.292	1		1.0771	3	
2.201	1		1.0456	2	
2.053	1		1.0243	2	511, 333
1.9976	6		0.9408	3	440
1.9569	2		0.8996	3	531
1.8842	35	220		$a=5.322$Å	

16) H. T. Hall and L. A. Compton, *Inorg. Chem.*, **4**, 1213 (1965)
17) B. R. Pamplin, *J. Phys. Chem. Solids*, **25**, 675 (1964)

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of B_2O requires 120kb, while that of ZnP_2 takes place only at 15kb.

The pseudo-cubic form of ZnP_2 has a measured density of 3.55g/cm^3, which is quite near to the values 3.47g/cm^3 of the monoclinic ZnP_2 and 3.536g/cm^3 of the tetragonal ZnP_2. In view of the density and the comparatively low transition pressure of ZnP_2, the pseudo-cubic ZnP_2 may have a similar chemical bonds and crystal structure to other modifications of ZnP_2, especially to the tetragonal ZnP_2. The high pressure modification has a metallic appearance at the cross section. It is pulverized easily and black in powder.

In the sphalerite (or diamond) structure there exist 8 atoms in a unit cell. Although 8 atoms can not be assigned to zinc and phosphorus in the atomic ratio 1 : 2, 24 atoms in three unit cells, for example, can be assigned to 8Zn and 16P atoms. Therefore, the high pressure modification would have a disordered sphalerite like structure in which zinc and phosphorus atoms are distributed statistically to the ratio, Zn : P = 1 : 2.

Electrical resistance measurements

The measurements of room temperature resistance *versus* pressure were carried out on the powdered samples of the monoclinic and the pressure-induced modifications (Fig. 2). The sample dimensions after the runs are about 1mm in length and 1mm × 1mm in area. Thus the resistivity is nearly equal to one tenth of the resistance. For pressures up to 40kb, the resistivity of monoclinic ZnP_2 gradually decreases with pressure and reaches to about 10^{-1} Ω-cm. The pressure-induced ZnP_2 exhibits almost similar behavior but has higher resistivity by 10^2 order of magnitude. The temperature dependences of the electrical resistance of high pressure modification under various pressures are shown in Fig. 3. The linear relationships are found between $\log\rho$ and $1/T$ in the temperature range from room temperature to 200°C.

For semiconductors the electrical resistance ρ, in the intrinsic region of conduction, is given by

$$\rho=\rho_0 \exp(E_g/2kT) . \qquad (1)$$

where E_g is the energy gap, k the Boltzmann constant, T the absolute temperature and ρ_0 an essentially temperature independent constant. Thus, the slope of $\log\rho$ *versus* $1/T$ curves yields the energy gap. On the hypothesis that the temperature range covered in the present work includes the intrinsic region of conduction, the energy band gap E_g is calculated. The values of E_g decrease gradually with pressure. By differentiating equation (1) and neglecting the smaller terms, the following equation is given to the intrinsic conduction of semiconductors.

$$\frac{\partial \ln\rho}{\partial P}\cong\frac{1}{2kT}\frac{\partial E_g}{\partial P} . \qquad (2)$$

Figs. 2 and 3 give the following experimental values for the pressure range from 15 to 35kb respectively.

$$\frac{\partial \ln\rho}{\partial P}\cong 2\times 10^{-5}\ \text{bar}^{-1} .$$

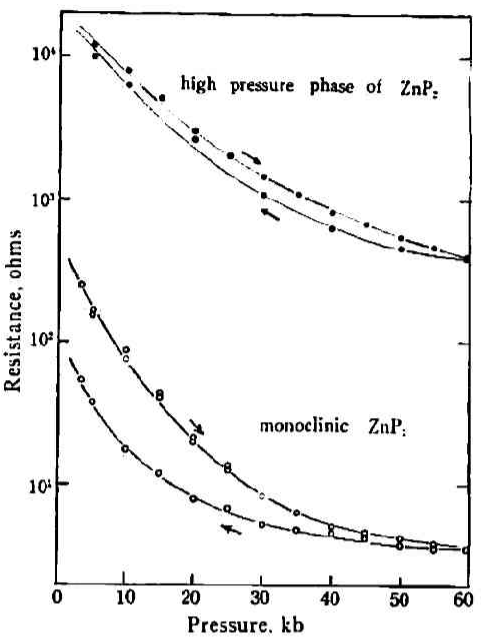

Fig. 2 Pressure dependences of room temperature resistance of monoclinic ZnP_2 and high pressure phase of ZnP_2

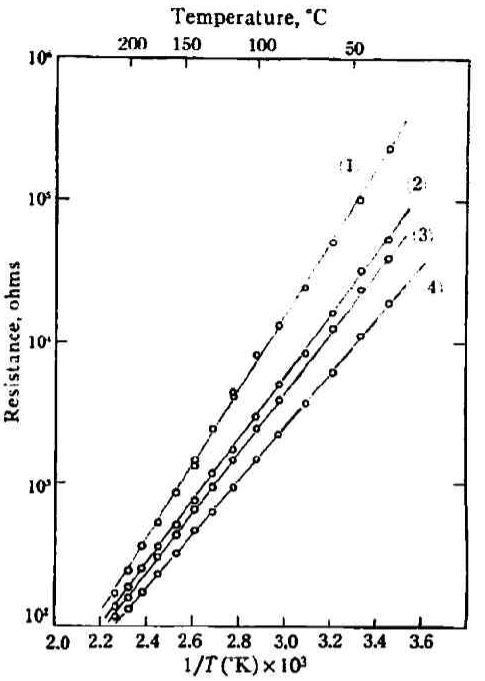

Fig. 3 Temperature dependences of electrical resistance of high pressure phase of ZnP_2 at pressures of:
(1): 15 kb, E_g=0.44 eV (2): 20 kb
(3): 25 kb (4): 35 kb, E_g=0.32 eV

$$\frac{1}{2kT}\frac{\partial E_g}{\partial P}=7.4\times10^{-5}\ \text{bar}^{-1}.$$

The order of these values is equal so that the observed decrease in resistance of pressure-induced ZnP_2 with pressure may be mainly due to the decrease in E_g with pressure.

The chemical properties of high pressure modification are similar to those of other two modifications. Pressure-induced ZnP_2 is attacked vigorously by aqueous HNO_3, but it is resistant to hot concentrated H_2SO_4, HCl, $HClO_4$, HF and NaOH.

Effects of temperature and pressure on the polymorphic transition of ZnP_2

The measurements on electrical resistance *versus* temperature were performed on the powdered sample of the monoclinic ZnP_2 in order to detect the transition by a discontinuous change of electrical resistance. The results are given in Fig. 4. According to White *et al.*[4], the monoclinic ZnP_2 has an optical energy gap E_g=1.33 eV for the electric vector of plane polarized light parallel to the *c*-axis and 1.37 eV for the light polarized perpendicular to *c*-axis. Judging from the intrinsic region of conduction for monoclinic $ZnAs_2$[18], which is the phase corresponding to the monoclinic ZnP_2, that for monoclinic ZnP_2 may be approximately 90~150°K. Therefore the measured conductivity is probably extrinsic.

18) W. J. Turner, A. S. Fischler and W. E. Reese, *Phys. Rev.*, **121**, 759 (1961)

As seen in Fig. 4, the decrease of the electrical resistance with temperature is considerably small. Although it is confirmed by X-ray diffraction that the monoclinic ZnP_2 transforms partially into the high pressure phase at about 150°C under 25 kb, any discontinuous change of electrical resistance can not be found in this experimental condition. It may be due to that the difference in resistivity between the monoclinic ZnP_2 and the high pressure modification is not large enough to be detectable at the required temperature and pressure since the resistivity of monoclinic ZnP_2 remains almost constant, 10 Ω-cm, while that of pressure-induced ZnP_2 decreases from 10^4 Ω-cm to 10 Ω-cm with temperature as seen in Fig. 3. Thus, the polymorphic transitions have been followed by the quenching method using X-ray diffraction. The calibration curves to determine the amounts of the monoclinic and the pressure-induced modifications were made by using ZnO as an internal standard. The (111) peak of pressure-induced ZnP_2, the (202) peak of monoclinic ZnP_2 and the (101) peak of ZnO were utilized for determination.

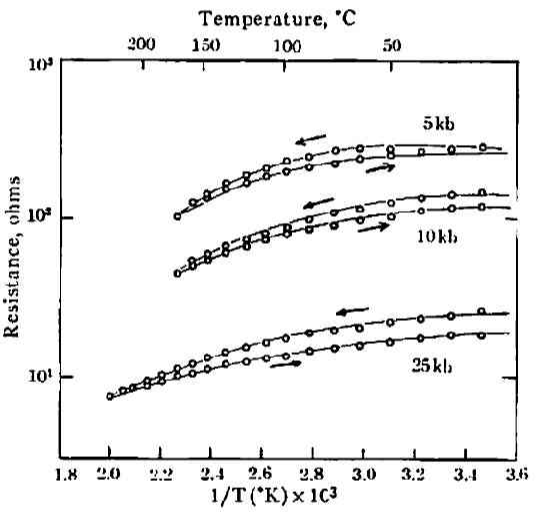

Fig. 4 Temperature dependences of electrical resistance of monoclinic ZnP_2

The monoclinic → pseudo-cubic transition of ZnP_2

In Fig. 5 is presented the plot of percentage conversion of the monoclinic ZnP_2 into the pseudo-cubic form *versus* time at 300°C under 20 kb. The transition proceeds mainly within the first 30 minutes and the rate of transition is very slow after then. Therefore, the effects of temperature and pressure on the phase transition have been investigated by measuring the per cent conversion in 60 minutes.

Fig. 6 shows the temperature dependence of percentage conversion for three pressures. The phase transition does not take place below 150°C under any pressure. At 30 kb the conversion increases considerably with temperature and reaches practically 100 per cent at 600°C. In Fig. 7 are shown the pressure dependences of percentage conversion for two temperatures. The phase transition requires pressures of 17.5 kb at 200°C and 13 kb at 300°C. It can not be achieved by raising temperature or pressure alone. In the pressure-induced modification prepared below about 17 kb, a small shift was found in the value of spacing of the (111) peak as compared with the spacing of the high pressure phase obtained under enough high pressure. The phase transition proceeding below 17 kb would yield an

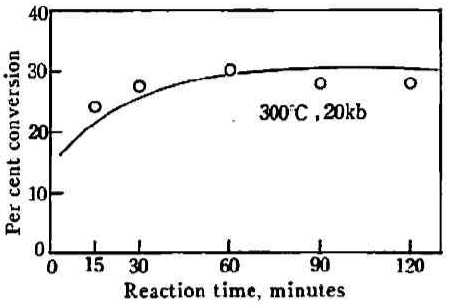

Fig. 5 Fraction of conversion completed *versus* time for monoclinic ZnP_2 → pseudo-cubic ZnP_2

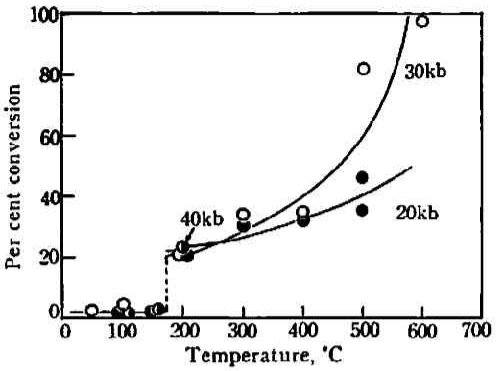

Fig. 6 Fraction of conversion completed *versus* temperature for monoclinic ZnP_2→pseudo-cubic ZnP_2

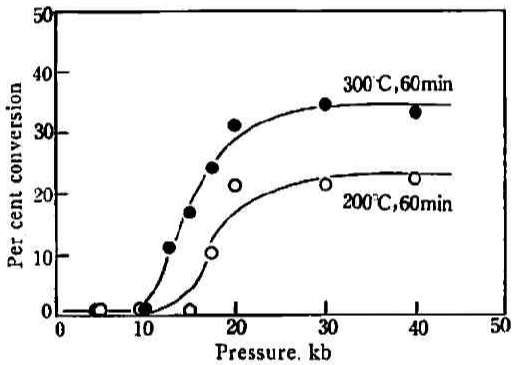

Fig. 7 Fraction of conversion completed *versus* pressure for monoclinic ZnP_2 → pseudo-cubic ZnP_2

intermediate phase between the monoclinic and the pseudo-cubic ZnP_2.

The tetragonal→monoclinic or pseudo-cubic transition of ZnP_2

The percentage conversion of the tetragonal ZnP_2 into the monoclinic form *versus* the time plot at 500°C under 10kb is presented in Fig. 8. The tetragonal ZnP_2 transforms only into the monoclinic form in this condition since the phase transition of the monoclinic ZnP_2 into the pseudo-cubic form does

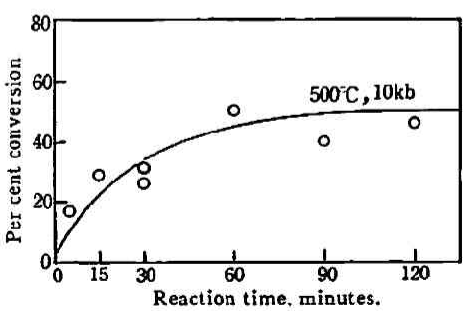

Fig. 8 Fraction of conversion completed *versus* time for tetragonal ZnP_2→ monoclinic ZnP_2

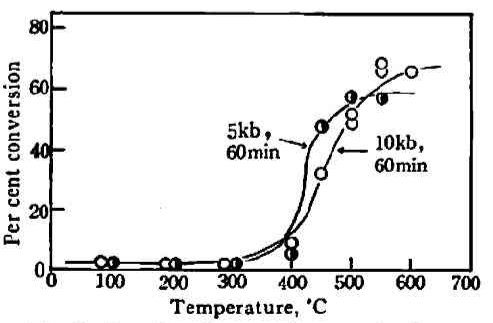

Fig. 9 Fraction of conversion completed *versus* temperature for tetragonal ZnP_2→monoclinic ZnP_2

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not take place. The transition proceeds mainly in the first 60 minutes. In Fig. 9 the percentage conversions are plotted against temperature for pressures of 5 and 10 kb. The transition requires the temperatures above 400°C and it is retarded by pressure since the tetragonal ZnP_2 has higher density and higher crystal symmetry as compared with the monoclinic modification. The leveling-off of the curves above 500°C may arise from the fact that the monoclinic ZnP_2 once formed transforms inversely into the tetragonal ZnP_2.

In the higher pressure range above 20 kb, the transition of the tetragonal ZnP_2 into the pseudo-cubic form also takes place. In opposition, pseudo-cubic form of ZnP_2 transforms gradually into tetragonal and monoclinic forms in the lower pressure region. Therefore the new phase may be a thermodynamically stable one. The stability region for the high pressure modification has been approximately determined by quenching as shown in Fig. 10. The phase boundary of monoclinic $\rightleftharpoons$ pseudo-cubic transition is rather ambiguous above 200°C at 10~20 kb on account of occurrence of an intermediate phase. The true boundary possibly exists in a little higher pressure region.

The stability relations among various phases of a substance are governed by their free energy. At a given temperature and pressure, the phase with the lowest Gibb's free energy is the stable one. At a phase boundary, the free energies of the two phases are equal. For a given substance, the phase with lower coordination and lower density is generally of higher entropy and lower symmetry and would be expected to be stable at higher temperature. On the other hand, the phase of higher coordination is of lower entropy and higher symmetry and would be expected to be stable at lower temperatures. However, ZnP_2 behaves differently. The tetragonal ZnP_2, the denser and more symmetric phase, is stable at high temperature. It is to be noted that the resistivity of the pressure-induced modification, $10^3\,\Omega$-

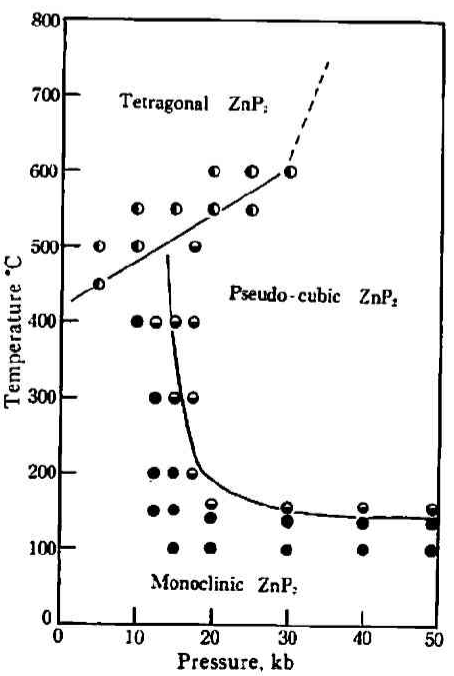

Fig. 10 *P-T* diagram of ZnP_2

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cm, is an intermediate value between $10^6\,\Omega$-cm of the tetragonal ZnP_2 and $10\,\Omega$-cm of the monoclinic ZnP_2.

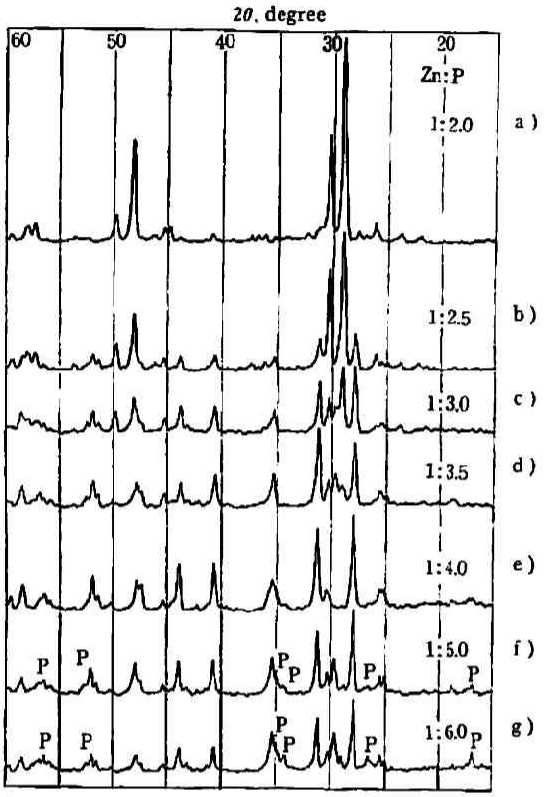

Fig. 11 The change of X-ray diffraction diagrams of the products with the increase of the atomic ratio of phosphorus in the starting mixture

Synthesis of a new crystalline form of ZnP_4 at high temperature and high pressure

According to the investigation of Renault[5] on the Zn-P system, amorphous ZnP_4 was obtained by treating a large amount of Zn_3P_2 with aqueous HCl, H_2SO_4 or HNO_3. Amorphous ZnP_4 was yellow, light and easily ignited. However, such compound could not be confirmed in this work. In the Cd-P[2] and the Mg-As[3] systems crystalline CdP_4 and $MgAs_4$ were prepared at normal pressure. Therefore, high pressure synthesis of crystalline ZnP_4 was undertaken in the present work.

In Fig. 11 are shown the changes of X-ray diffraction diagrams of the products with the increase of the atomic ratio of phosphorus in the starting mixture. The atomic ratio of phosphorus to zinc were changed from Zn : P=1 : 2 to 1 : 6 as seen in the figure. All experiments were carried out in the same experimental condition of 1,000°C and 40 kb for 2 hours.

As mentioned above, in the Zn : P=1 : 2 starting mixture only the pseudo-cubic ZnP_2 is prepared. With the increase of the ratio of phosphorus, however, new reflections appear besides those of ZnP_2 as seen in (b) and (c) and all reflections become considerably weak as compared with (a). This indicates that the specimen consists of more than two phases. The new reflections can not be assigned to black phosphorus which may be produced from red phosphorus through the phase transition under pressure. The reflections due to the pseudo-cubic ZnP_2 disappear completely in the Zn : P=1 : 4.0 sample. In

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the presence of excess phosphorus in such cases as (f) and (g), the reflections due to black phosphorus are found in addition to the reflections seen in the specimen (e). It indicates that the starting mixture in (f) and (g) may have excess phosphorus which is not concerned with the reaction. Consequently, the X-ray diffraction diagrams (e) may be assigned to the crystalline modification of ZnP_4. The indexing is not possible at this stage. Only the spacings and relative intensities are listed in the following table.

Table 4 Data of X-ray diffraction diagrams for the pressure-induced ZnP_4

d (Å)	I/I_0	d (Å)	I/I_0
3.477	20	1.9141	25
3.181	100	1.8962	30
2.936	25	1.7696	15
2.861	100	1.7554	25
2.532	35	1.6240	15
2.210	35	1.5734	20
2.061	35	1.5458	10
1.9965	10		

The pressure-induced ZnP_4 has a similar metallic appearance and chemical properties to the high pressure phase of ZnP_2. The color is black in powder. Exact stoichiometric composition, crystal structure and physical properties of this compound must be investigated in detail in the future.

Considerations

The author has described the new polymorphic transition of ZnP_2. It should be noted that this transition occurs only at high temperature and high pressure and produces a new quenchable high pressure modification. In order to synthesize new materials under high pressure, it is worth-while to review systematically the inorganic reactions undertaken at high temperature and high pressure.

A series of inorganic reactions between two elements which proceed very slowly at atmospheric conditions have been investigated at high temperature and high pressure since 1964 by using the compact cubic anvil apparatus constructed by Osugi *et al.*[11] A systematic prospect on the simple inorganic reactions at high temperature and high pressure will be presented on the basis of our experimental results.

Investigations of inorganic reactions under high pressure can be broadly classified into quantitative studies of the effects of pressure on the reaction rates and the discovery of new phases which can be produced only by pressure. The works of the former kind essentially use the pressure as an experimental parameter which may be varied at will. In the latter case, the pressure is used to produce a new phase, possibly possessing quite different physical and chemical properties. The discovery of new phases will be mainly considered here.

Formation of normal valence compounds

Formation of III-V compounds (B-P and B-As systems): III-V, II-VI and I-VII compounds are isoelectronic with group IV elements and have cubic sphalerite or hexagonal wurtzite structures.

BN, for example, is completely isoelectronic with carbon. This compound is found in a hexagonal layer-lattice form related closely to graphite in normal condition. The behavior of BN under high pressure is quite similar to that of carbon. Graphite-like BN is converted to a sphalerite form and a wurtzite form, which correspond respectively to the cubic and the hexagonal diamonds, at high temperature and high pressure[19)~21)]. To synthesize these materials high pressure is indispensable.

On the other hand, high pressure is not necessarily needed to synthesize any of known symmetrical group IV analogs other than two high pressure modifications of BN. It is, however, easily predicted that the application of high pressure to the reactions between two elements, one of which has comparatively low reactivity and high melting temperature and the other is very volatile, makes the reaction effective. From this point of view, the effects of high pressure on both the reaction of boron with phosphorus[10)] and that of boron with arsenic[12)22)] were investigated.

In these systems, the reactions are considerably accelerated by pressure below about 20 kb and simple normal valence compounds, cubic BP and BAs are obtained. The phases obtained at high pressures below 50 kb are just the same as the atmospheric phases. However, the decomposition of BP into $B_{13}P_2$ at high temperature is not found under high pressure.

Formation of IV-IV compound (Si-C system): The reaction of carbon with silicon was undertaken at temperatures of 700~1,400°C under pressures of 10~50 kb[23)]. At atmospheric conditions the reaction is usually undertaken in the higher temperature range above the melting temperature of silicon, 1,400°C and the product often contains a very small amount of hexagonal α-SiC intermixed in the sphalerite type β-SiC. On the other hand, the reaction sets out at about 800°C under 10~30 kb. In this condition both silicon and carbon are just in the solid state. β-SiC is the only product of the reaction under high pressure. The reaction finished almost instantaneously above the melting temperature of silicon.

As mentioned above, the application of pressure may serve to speed up or slow down certain reactions whose rates at normal conditions are too low or too high to be conveniently studied.

Although there are many examples of the phase transition of inorganic compounds which take place only at high pressure, the atoms which never react originally at the ordinary pressure but begin to react under high pressure have not so far been known in the lower pressure range below 50 kb as far as the author knows. For instance, in the B-Sb and the B-Bi systems, the cubic BSb and BBi were never recovered to atmospheric conditions in our experiments. At very high pressures above a million bars, however, it is possible that the energies of compression may become comparable with chemical bonding energies. Many new electronic energy state will be made available to the original valence electrons. Therefore, new high pressure chemistry will be considerably different from the chemistry under milder conditions.

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Even if the required objects could be composed in such conditions, some of them can not survive the decompression to the normal condition because of the mechanical irrationalities ascribed to the differences in atomic size, the effective atomic charge and the valence properties of component atoms.

Directionally-bonded normal valence compounds have relatively strong chemical bonds, high melting or sublimation temperature and high hardness. Therefore, they hardly transform into new high pressure form below 50kb. However, by analogy with group IV elements, these compounds will collapse to metallic forms at very high pressure above about 200kb.

Formation of anomalously composed semiconductors

The regular valence rule is generally observed with few exceptions in the pressure range employed in the laboratory. The energies which may be added to matters by compression is 1～2kcal/g·mole by being compressed to 100kb. Such compression energies are very small as compared with those of chemical bonds *i.e.* 20～80kcal. However, it is evident that the energy supplied by compression produces quite different effects from those due to the thermal energy. Pressure creates situations unattainable only by thermal means. Thermal treatments do not usually modify the structure of the electron shell; it simply changes the distribution of the electrons on the levels. On the other hand, the application of very high pressure together with high temperature may change the order of the levels. Thus, in order to discover new high pressure modifications in comparatively low pressure range below 100kb, it is desirable to attack the materials with comparatively weak chemical bonding, lower crystal symmetry and larger compressibility, for example, the materials with layer structure, molecular crystals and so on.

From this point of view, it is worth-while to apply very high pressure to the anomalously composed semiconductors[6)7)]. The crystal structures of anomalously composed phases, whose compositions differ from those expected from the normal valence rule, are much complicated and very low in crystal symmetry, since they have some anion-anion or cation-cation bonds besides cation-anion bonds. It is therefore expected that considerable pressure effects will come out when these reaction systems are undertaken at high temperatures under very high pressures since high pressure makes higher the co-

Table 5 Examples of anomalously composed semiconductors

System	Examples
I-V	CuP_2, $CuAs_2$?, AgP_2, $AgAs_2$?
II-V	MgP, MgAs, ZnP?, ZnAs?, ZnSb, CdP?, CdAs?, CdSb MgP_4?, $MgAs_4$, ZnP_2, $ZnAs_2$ CdP_2, CdAs ZnP_4?, $ZnAs_4$? CdP_4, $CdAs_4$?
IV-V	SiP, SiAs, GeP, GeAs, SnP SiP_2, $SiAs_2$, GeP_2?, $GeAs_2$, SnP_2?
III-VI	GaS, GaSe, GaTe, InS, InSe, InTe
IV-VI	SiS, SiSe, SiTe, GeS, GeSe, GeTe, SnS, SnSe, SnTe, PbS, PbSe, PbTe
V-VI	AsS, AsSe, SbSe, BiSe

The question mark indicates that the corresponding phase is likely to exist.

ordination number in the crystal and the crystal symmetry. Anomalously composed semiconductors have generally lower melting temperature, lower hardness and more metallic nature as compared with the normal valence semiconductors. They have not any absolute resistances to chemical reagents especially to oxidizing reagents.

The examples of anomalously composed semiconductors are listed in Table 5. In any systems in the table the rate of formation of these compounds at atmospheric pressure is very small so that even the physical and chemical properties of atmospheric phases have not so far been investigated sufficiently.

The examples of the simple inorganic reaction betwen two elements in which some unique and interesting pressure effects are found are listed in Table 6. In any systems the rate of reaction is very

Table 6 Examples of inorganic reactions at high temperature and high pressure

System	Atmospheric phase Products	Structure	High pressure phase Products	Structure	Condition of formation Temperature (°C)	Pressure (kb)	References
III-V							
B-N	BN	hex	BN	cub-ZnS	1,700~2,200	60~90	19, 20
			BN	hex-ZnO	room temp.	140	21
B-P	BP	cub-ZnS	BP	cub-ZnS	1,000~1,400	5~15	10
	$B_{13}P_2$	rhomb					
B-As	BAs	cub-ZnS	BAs	cub-ZnS	800~1,100	5~40	12
	$B_{13}As_2$	rhomb	$B_{13}As_2$	rhomb	1,200~1,400	5~40	
IV-IV							
Si-C	α-SiC	hex	β-SiC	cub-ZnS	700~1,400	10~50	23
	β-SiC	cub-ZnS					
II-V							
Zn-P	Zn_3P_2	tet	Zn_3P_2	tet	150~400	5~50	15
IV-V							
Si-P	SiP		SiP	cub-ZnS	1,400~1,500	40~50	8
	SiP_2	ortho	SiP_2	cub-FeS_2	1,000~1,400	3~40	
Si-As	SiAs	mon	$SiAs_2$	cub-FeS_2	1,100~1,300	45~55	24
	$SiAs_2$	ortho					
Ge-P	GeP	mon	GeP	cub-ZnS	1,400	40	9
			GeP	disordered-ZnS	1,350	40	
			GeP_2	cub-ZnS	1,000~1,200	30~40	
Sn-P	SnP	hex	SnP	cub-ZnS	1,700	40~50	9
II-V							
Zn-P	ZnP_2	mon	ZnP_2	mon	300~600	5~15	This
	ZnP_2	tet	ZnP_2	tet	600~1,000	5~20	work
			ZnP_2	pseudo-cub	150~	15~	
III-VI							
In-Te	InTe	tet	InTe	cub-NaCl	400~500	30	25
B-O	B_2O_3	hex	B_2O_3	mon	400~700	22~30	26
			B_2O	hex	1,200~1,800	50~75	16
			B_2O	cub	1,200~1,800	120	16

(continued on the next page)

(Table 6 continued)

IV-VI							
Si-S	SiS_2	ortho	SiS_2	tet	700～1,500	50～75	27, 28
Ge-S	GeS	ortho	GeS_2	tet	1,100	45	
	GeS_2	ortho					
V-VI							
Bi-S	Bi_2S_3	ortho	BiS_2	?	1,250	50	29
Bi-Se	BiSe	cub-NaCl	$BiSe_2$	?	1,300	45	30
	$BiSe_2$	rhomb	BiSSe	?			
I-VI							
Cu-S	CuS	hex	CuS_2	cub-FeS_2			
Cu-Se	CuSe	hex	$CuSe_2$	cub-FeS_2	400～	30	31, 33
Cu-Te	CuTe	ortho	$CuTe_2$	cub-FeS_2			
II-VI							
Zn, Cd – S, Se, Te	ZnS (AB)	cub-ZnS hex-ZnO	ZnS_2 (AB_2)	cub-FeS_2	800～1,200	65	
VIII-V							
Fe, Co, Ni – P, As	NiAs	hex	$NiAs_2$	cub-FeS_2	1,400	60	32, 33
	FeP (AB)	ortho	FeP_2 (AB_2)	cub-FeS_2			
VIII-VI							
Ir-S	IrS_2	ortho	IrS_2	cub-FeS_2	1,500	60	32

low at atmospheric pressure.

Formation of IV-V compounds (Si-P[8], Ge-P[9] and Sn-P[9] systems): In the Si-P system, yellow SiP was prepared in 1938 by reacting silicon with phosphorus directly in a sealed silica tube above 1.000°C in the presence of catalyst Tl[34]. Recently Schmidt and Stickler[35] have suggested the presence of an orthorhombic SiP in the surface layer of heavily phosphorus diffused silicon. However, SiP_2 which is likely to exist in view of the corresponding phases of $SiAs_2$ and $GeAs_2$ has not so far been confirmed. Therefore, the reaction of silicon with phosphorus was undertaken at temperatures of 1,100～1.800°C under pressures of 10～50kb in order to get informations of the effects of very high pressure on the crystal structure of the anomalously composed SiP and to try the high pressure synthesis of SiP_2.

The X-ray diagrams taken after releasing the pressure showed that five kinds of new crystalline phases were prepared in the Si-P system[8]. Among these new phases a cubic pyrite type SiP_2 with a

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lattice constant of 5.682Å and a cubic sphalerite type SiP with a lattice constant of 5.241Å are included. Pyrite type SiP_2 prepared at 1,100~1,500°C under 20~40kb has a metallic appearance and it is black in powder. Sphalerite type SiP is found only above 1,500°C under 40~50kb. SiP is metallic and black in powder.

Recently the pyrite type SiP_2 has also been synthesized in an evacuated silica tube with enough halogen to produce 2~3 atmosphere pressure at about 800°C by Donohue *et al.*[34] The room temperature electrical resistivity is in the range of 3×10^{-5}~$3\times10^{-4}\Omega$-cm. They have also succeeded in synthesizing a pyrite type $SiAs_2$ with a lattice constant 6.0232Å at 1,300°C under 45~55kb. High pressure is indispensable to prepare this phase.

It should be noted that SiP_2 and $SiAs_2$ are the only examples of pyrite type compounds of non-metallic elements. They are also unusual in that silicon is in octahedral coordination.

In the Ge-P system, a monoclinic GeP[36] was prepared in 1939 by direct union of germanium and phosphorus at about 700°C in an evacuated silica tube for about 10 days. SiP and GeP obtained at atmospheric conditions are not the phases corresponding mutually in view of the crystal structure and chemical property. Thus, the reaction of germanium with phosphorus was undertaken at 600~1,500°C under 10~15kb in order to compare the system with the Si-P system[9].

Eight kinds of crystalline phases and other several numbers of non-indexed reflections were revealed by X-ray analysis. Among these new phases a disordered sphalerite type GeP with a lattice constant of 5.463Å are included. The sphalerite type GeP is the phase corresponding to the SiP stated above. However, the high pressure phase which corresponds completely to the pyrite type SiP_2 is not confirmed in the Ge-P system.

The change of crystal structures of high pressure phases with pressure is much more complicated in the Ge-P system than that in the Si-P system. It may be due to the higher metallic nature of germanium as compared with silicon.

It was confirmed that a sphalerite type SnP[9] with a lattice constant of 5.544Å was prepared at about 1,700°C under 40~50kb. This may be the phase corresponding to the sphalerite type SiP and GeP.

The sphalerite type SiP, GeP and SnP are unusual in the fact that the average number of valence electron per atom is not 4.

Formation of unsymmetrical group IV analogs (Zn-P system): The synthesis of a diamond-like form of ZnP_2 was stated in the present work. It was also confirmed that the monoclinic $ZnAs_2$ transforms into a new high pressure phase above 10kb at 100°C. The high pressure modification may not be similar to the pseudo-cubic form of ZnP_2.

As mentioned above, very high pressure often induces very interesting changes of crystal structures of anomalously composed semiconductors. It would be mainly due to the weakness of chemical bonds and the decrease of the directional character. Most of high pressure modifications of anomalously composed semiconductors can be recovered to the normal conditions.

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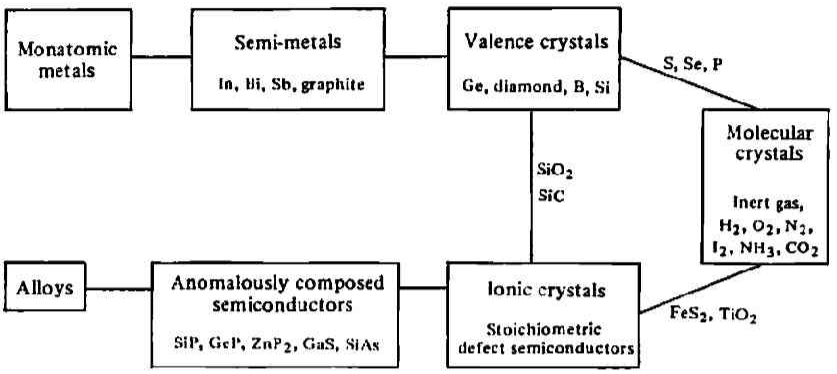
Anomalously composed semiconductors are interrelated to other solid types as shown in the following schematic diagram. Molecular crystals have low densities since the intermolecular cohesion

The interrelation of the solid types



is weak so that the corresponding interatomic distances are large. In valence crystals, atoms can be described as connected up by a three-dimensional net work of chemical bonds, which leads to relatively high density and hardness. In the crystal structures with greater coordination numbers, a unique valence structure cannot always be written and metallic behavior is found.

According to the thermodynamic principle, the application of pressure will tend to produce or accelerate transitions to phases of higher density in the direction from right to left in the diagram. A metallic state is probably the ultimate fate of all materials if the pressure is sufficiently high.

Anomalously composed semiconductors have so far only scarcely been investigated and so they represent a large and challenging field to the solid state physicist and the high pressure researcher.

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